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UNUSUAL POLYHALOGENATED CHEMICAL RESIDUES IDENTIFIED IN FISH TISSUE FROM THE ENVIRONMENT

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ABSTRACT

A review of polyhalogenated xenobiotic chemicals identified in fish obtained from environmental sampling is presented. The review does not include chemicals routinely reported in pesticide and polychlorinated biphenyl monitoring, nor chemicals studied in fish bioassay experiments.

INTRODUCTION

One of the more important procedures used to evaluate man's effect upon the environment is chemical-residue determination. In particular, the identification and quantification of xenobiotic chemicals in fish result in a direct measure of persistent hazardous synthetic organic chemicals associated with industrial and agricultural activities in a specific watershed.

The analysis of chemical residues in fish can follow one or both of two approaches: chemical-residue monitoring and chemical-residue characterization. Chemical-residue monitoring is the determination of levels of a known chemical(s) in the fish from a specific watershed(s) over a designated time period. In this case a statistical approach to the analysis is used to determine trends in chemical residues. In contrast, chemical-residue characterization is the isolation, identification, and, if possible, quantification of unknown xenobiotic chemicals accumulated in fish tissue. This exploratory approach is used to determine what chemicals actually can be found as persistent residues. Often new analytical

techniques of compound isolation and identification must be developed to characterize residues successfully. Jung and Bowes (1) have pointed out that "what we know of toxic substances in the environment is very much dependent on the limitations of current analytical capabilities," and therefore methodology development is a very important part of the overall approach to chemical-residue characterization.

The purpose of this paper is to review findings of unique or unusual polyhalogenated xenobiotic chemicals identified in fish from the environment during 1970-80. The review will therefore deal with papers on chemical residue characterization and will not discuss papers on routine chemical-residue monitoring or papers describing laboratory bioassay experiments with fish.

POLYHALOGENATED CHEMICALS IDENTIFIED IN FISH

A multicomponent mixture of polychlorinated styrenes (PCS) consisting mainly of hexachloro- and heptachloro- isomers and octachlorostyrene has been identified as a chemical residue in fish from both European and North American waters. Specifically, these substances have been found in fish from Lake Ontario, Lake Huron, and the Detroit River (2, 3); the Ashtabula River in Ohio (3, 4, 5); the Saginaw River in Michigan (3, 4); and the fjords of Norway (6, 7). The first report of octachlorostyrene in the environment came from the Rhine River in the Netherlands (8) where it was originally detected in eider ducks (Somateria mollissima) and sandwich terns (Sterna sandvicensis) and was detected later in seals (Phoca vitulina), cormorants (Phalacrocorax carbo), and fish (9). Polychlorinated styrenes are not commercially produced, but appear to arise as a by-product in industrial processes involving high temperature carbon-chlorine reactions. The contamination of the Norwegian fjords resulted from the formation of PCSs as byproducts in an industrial process converting magnesium oxide to magnesium chloride (10). No source has been given for PCSs in the United States, although the production of chlorine gas by using carbon electrodes has been suggested as a possible source (11).

The compound 2-chloroaniline, a contaminant in methylene bis(2-chloroaniline), was found in fish from the Raisin River at Adrian, Michigan, near the discharge of a municipal wastewater treatment plant (12). Methylene bis(2-chloroaniline), used to cure urethane and epoxy resins, was not detected in these same fish partially because of poor recoveries during sample cleanup.

Methylthiopentachlorobenzene and di-(methylthio)tetrachlorobenzene have been reported in mussels (Mytilus edulis) from Dutch coastal waters (13). The source of these two sulfur-containing compounds is thought to be the metabolism of pentachloronitrobenzene (PCNB, also known as Quintozene or Tetraclor) by plants (14, 15). PCNB is used in the Netherlands as a fungicide on lettuce and other greenhouse plants.

Dimethyltetrachloroterephthalate (DCPA) has been detected in five species of fish from the Arroyo Colorado in the Rio Grande Valley in Texas (16). DCPA is used as a pre-emergence herbicide on onion, cabbage, and cotton crops.

A complex mixture of chlorofluorotoluenes was identified as a residue in Niagara River, New York, fish (17). Five compounds specifically identified were: 4-chloro-α,α,α-trifluorotoluene; 2-chloro-α,α,α-trifluorotoluene; 3,4-dichloro-α,α,α-trifluorotoluene; 2,4-dichloro-α,α,α-trifluorotoluene; and 2,3-dichloro-α,α,α-trifluorotoluene. In addition, 2,6-dichlorotoluene and 2,4,5-trichlorotoluene were also identified in these fish. Fish from Lake Erie were also analyzed for these same compounds, but none were detected. Pentachlorotoluene was previously reported as a residue in Lake Ontario fish (18). The source for the chlorofluorotoluenes was not determined, but monochloro-α,α,α-trifluorotoluenes are used as solvents and in making chemicals dyes, pesticides, and pharmaceuticals, while dichloro-α,α,α-trifluorotoluenes and chlorinated toluenes are used as intermediates in manufacturing agricultural chemicals.

The compounds 1,2,3,4,7,7-Hexachloro-2,5-norbornadiene (HCND), 1,2,3,4,5-endo-7,7-heptachloro-2-norbornene, and 1,2,3,4,7,7-hexachloro-5,6-endo-epoxy-2-norbornene (HCEN) have been identified as contaminants in fish from the Mississippi River near Memphis, Tennessee; Geismar, Louisiana; and Baton Rouge, Louisiana (19); and in fish from the Wabash River near Terre Haute, Indiana (4). The first and second of these compounds are used as intermediates in the production of the insecticide endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endro-1,4-endo-5,8-di-methanonaphthalene). The compound HCEN arises from the environmental oxidation of the HCND compound.

Polychlorinated dibenzo-p-dioxins (PCDDs) have been the subject of much interest because of the extreme toxicity of the 2,3,7,8-tetrachloro isomer (TCDD). This chemical was reported in Vietamese fish collected in 1970 at levels as high as 800 ppt (20, 21), but, samples collected in 1973 did not contain TCDD at 20-50 ppt (22). No PCDDs could be detected at 10-40 ppt in a white shark (Carcharodon carcharias) caught off Deer Island on the New Brunswick, Canada, coast, or in pickerel (Esox niger) and eel (Anguilla rostrata) from the St. John River, New Brunswick, Canada (23). The compound TCDD was not detected in catfish and bass (species not specified) collected from a Grady, Arkansas, pond nor in catfish or walleyed pike collected from the San Angelo, Texas, reservoir (24). The detection limit for this study was 5-14 ppt. Both the Texas and Arkansas sites were agricultural areas where 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) is used extensively as a herbicide. Thirteen fish samples collected between 1970 and 1977 from the Ohio River at Cincinnati and Marietta, Ohio; Lake Michigan at Saugatuck, Michigan, and Sheboygan, Wisconsin; the Hudson River at Wappinger Falls, New York; the Connecticut River at Wilson, Connecticut; and the Tittabawassee River at Dow Dam and Emerson Park (Midland), Michigan; and a sediment sample from Lake Michigan at Waukegan, Illinios; a snapping turtle from the Hudson River, New York; and a seal from the Gulf of Bothmita, Baltic Sea, were all analyzed for PCDDs by negative chemical ionization mass spectrometry (25, 26, 27). Isomers of tetra-, penta-, hexa-, hepta-, and octachlorodibenzo-p-dioxin were found above approximately 500 ppt in only two of these samples, fish from the Tittabawassee River at the Dow Dam and Emerson Park sites in Midland, Michigan. The compound TCDD was estimated to be 1000 ppt in these samples.

The polychlorinated dibenzofurans (PCDFs), compounds similar in structure to the PCDDs, have also been identified as residues in fish. Some PCDFs similar in composition to those found as contaminants in commerical PCBs were identified in fish taken between 1970 and 1977 from the Ohio River near Cincinnati and Marietta, Ohio; Lake Michigan near Saugatuck, Michigan; the Connecticut River, Connecticut; and the Hudson River, New York (27, 28, 29). Concentration estimates based upon negative chemical ionization mass spectrometry were 0.5 - 5.0 ppb. No PCDFs were observed in pickerel and eel from the St. John River, New Brunswick, Canada, or in white shark caught off Deer Island on the New Brunswick coast (23). A trichlorodibenzofuran and two possible precursors, a trichlorodiphenyl ether and a tetrachlorodiphenyl ether, were identified in lobster (Homarus americanus), mussel (Mytilus edulis), and clams (Mercenaria mercenaria) (28) caged in northern Narragansett Bay, Rhode Island, during 1978. No quantitative data were given.

Polychlorinated naphthalenes (PCNs) of 4, 5, 6, and 7 chlorine were identified in 13 fish samples from the Ohio River at Cincinnati, Ohio, 1970 and 1974, and at Marietta, Ohio, 1970, 1971, and 1974; Lake Michigan at Saugatuck, Michigan, 1974, and at Sheboygan, Wisconsin, 1974; the Connecticut River at Wilson, Connecticut, 1970 and 1974; the Hudson River at Wappinger Falls, New York, 1974 and 1976; and two sites on the Tittabawassee River, Emerson Park and Dow Dam at Midland, Michigan, 1977 (25, 26, 27). Concentration estimates were 0.5 - 5.0 ppb. Polychlorinated biphenyls were reported at a level of 39 ppb in a dead fish found upstream from a PCN manufacturing plant, but no details on the location of the site of collection were given (29). Pentachloro and hexachloro naphthalenes were also identified in fish from Norwegian fjords (7), but they were not quantified.

Several polybrominated chemicals were identified by gas chromatography/mass spectrometry (GC/MS) in fathead minnows (Pimephales promelas) exposed to wastewater-treatment-plant discharges at Grandville and Wyoming, Michigan (30). Specifically bromoindole, dibromoindole, tribromoindole, tetrabromoindole, dibromomethylindole, tribromomethylindole, tetrabromomethylindole, dibromomethylbenzthiazole, dibromophenol, tribromophenol, chlorobromophenol, dichlorobromophenol, dibromomethylphenol, dibromoanisole, and tribromoanisole were all identified as residues in fish that were exposed to effluent that had been disinfected with bromine chloride, but not in fish exposed to chlorinated, ozinated, or nondisinfected wastewater. Similar compounds have been identified in marine hemichordates. The acorn worm (Balanoglossus biminiensis), which lives along coastal areas of southern United States, contained 2,6-dibromophenol (31). Another acorn worm (Ptychodera flava), collected at Paiko Beach, Hawaii, contained 2,4,6-tribromophenol, 3-bromoindole, 3-chloro-6-bromoindole, and 3-chloroindole (32, 33). The breakdown of tryptophan in a halide environment was suggested as a possible source.

Trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-di-n-propyl-p-toluidine), a herbicide, was studied extensively in the fish population of the Wabash River at Lafayette, Indiana (34). Eleven species of fish were caught between January and July 1974 from approximately 30 km above to 65 km below an industrial plant discharging trifluralin. Mean residue levels

(expressed as milligrams per kilogram of fat) ranged from 440.1 in golden redhorse (Moxostoma erythrurum) near the discharge to 0.3 in sauger (Stizostedion canadense) 32 km above the discharge.

Hexachloro-1,3-butadiene (HCBD), a byproduct from the synthesis of perchloroethylene, has been found as a residue in fish from both European and North American waters. Seven species of fish from the Ketelmoer, an inland body of water fed by the Rhine River, Netherlands, contained levels up to 1.86 ppm total in pike perch (Stizostedion hucioperca) during 1972. As a result of HCBD contamination of a large number of cattle in the lower Mississippi River basin in 1973, the U.S. Food and Drug Administration began an investigation of HCBD levels in fish from the lower Mississippi River including the flow area into the Gulf of Mexico (35). Six species of fish collected from the Mississippi River at Baton Rouge, Louisiana; Plaquemine, Louisiana, Geismar, Louisiana; and Freeport, Texas, contained HCBD at concentrations ranging from 0.01 to 1.20 ppm (36). HCBD was also identified in fish from the Ashtabula River, Ohio, 1976 (3); the Niagara River, New York, 1976 (17); and Lake Ontario, 1972 (37); but no quantification data were given for these studies. In addition to HCBD the Ashtabula River samples contained a series of similar compounds, specifically monochloro- through pentachloro alkanes and alkenes of two to five carbons (4, 5).

Trichloropropylamine, tetrachloropropylamine, and tetrachlorobutylamine were identified by electron impact and negative chemical ionization GC/MS in fish from the Ashtabula River, Ohio (4, 5), but no source for these compounds or quantification data were given.

The compound 1,3,5-trichloro-2-(4-nitrophenoxy)benzene (CNP), a widely used herbicide in Japan on rice fields, was isolated from mussels (Mytilus edulis) collected near Chiba Central Port along Tokyo Bay, Japan, in 1977 (38). The level of CNP in the mussel sample was 1 ppm, wet weight. This compound and an analogue, 1,3-dichloro-2-(4-nitrophenoxy)benzene (NIP), were later found by Yamagishi et al. in fish (Acanthogobius flavimanus) and short-necked clams (Tapes japonica) also collected in Tokyo Bay (39). The compound CNP was again reported in fish from Tokyo Bay, Japan, in 1979 when it was detected in rainbow trout imported to the United States (40). Levels of CNP in the edible portion ranged from 0.2 to 2.2 ppm.

Polychloro-2-(chloromethylsulphonamide)diphenyl ethers (PCSDs) have been used as alternatives to dieldrin as mothproofing agents in the textile industry. Methods were developed for their isolation and identification on pike (Esox lucius), perch (Perca fluviatilis), and brown trout (Salmo trutta) taken from an area in Great Britain where PCSDs were known to be used (41), but no details of sampling location or quantities were reported. Two metabolic products of PCSDs, 2',3,4,4',5,6-hexachloro-2-aminodiphenyl ether were identified in pike (Esox lucius) and eel (Anguilla anguilla) caught downstream from textile factories in the Viskan watershed, Sweden (42). The highest level found for the sum of the two metabolites was 0.4 ppm in eel.

The compound 2,4,6-trichlorophenol (TCP), isomers of trichloroguaiacol (TCG) and tetrachloroguaiacol (TeCG), which have been identified from kraft pulpmill bleach effluents as toxic components to rainbow trout (Salmo gairdneri) (43, 44), have been studied for bioaccumulation both in the laboratory and in the field (45). The substances TCP, TCG, and TeCG were all found in rainbow trout exposed in the laboratory to a pulpmill effluent and were also present in perch (Perca fluviatilis) and pike (Esox lucius) caught in a river near the vicinity of the pulpmill. In addition tetrachlorocatechol, which was thought to be a metabolite of the corresponding guaiacol, was detected in the liver of rainbow trout 8 weeks after discontinuation of exposure to the effluent.

Trichlorophenol was also identified in fathead minnows (Pimephales promelas) that had been exposed to experimental municipal waste-treatment-plant effluents from Grandville and Wyoming, Michigan (46). In addition, these fish contained dichlorobenzene, trichlorobenzene, tetrachlorophenol, tetrachloroanisole, pentachlorophenol, pentachloroanisole, trichloropropylmethoxynaphthalene, and tetrachloropropylmethoxynaphthalene as well as PCBs and DDTs. Since all of these compounds were found in fish exposed to either chlorinated or nondisinfected effluent it was assumed that these chemicals were a part of the wastes the plant was receiving and were not a result of aqueous chlorination. No quantitative data were given.

Pentachlorophenol (PCP), a herbicide, fungicide, insecticide, and bactericide, has a broad spectrum of industrial, agricultural, and home uses. Interest in this compound culminated in a conference in 1977 (47) where the metabolism of PCP in fishes was one of the topics (48). Pentachlorophenol was found in fish (species not specified) from a small man-made lake near Hattiesburg, Mississippi when the wastewater effluent from a wood-treating company overflowed into the lake in 1974 (49). Immediately after the spill concentrations were as high as 2,500 ppb, but dropped to background levels in 6 months. Pentachlorophenol was found in winter flounder (Pseudopleuronectes americanus) (1.77 ppb) and (Gadus morhua) (0.82 ppb) from the St. Croix estuary, New Brunswick, in 1972; in winter flounder (3.99 ppb) and silver hake (Merluccius bilinearis) (1.75 ppb) from the St. John estuary, New Brunswick, in 1972; and in the liver of a white shark (Carcharodon carcharias) (10.83 ppb) landed in Leonardville, New Brunswick, in 1971 (50). The structurally similar compounds polychlorinated phenyl phenols, which are metabolites of PCBs (51), were also found in these same Canadian samples, but were not quantified. Pentachlorophenol has been found in fish from the Wabash River, Indiana (41).

The methylated derivative of pentachlorophenol, pentachloroanisole (PCA), has been found in fish from the Detroit River, Michigan (3), and in fish from 15 of 26 rivers sampled near the Great Lakes (5). Lower chlorinated anisoles have been found along with PCA in fish from the Arkansas River, Arkansas (3), and in fish exposed to sewage outfall (46). No quantitative data were given.

Dichlorobenzophenone, a metabolic product of p,p'-DDT, was identified by GC/MS in Lake Michigan trout (52). No quantitative data were given.

Hexachlorobenzene, a commonly monitored toxicant, has been measured at levels greater than 5 ppb in fish from 29 of 58 United States watersheds in 1976 (3), and 17 of 29 watersheds studied in 1978 (4). More interestingly, however, during these exploratory studies isomers of dichloro- through pentachlorobenzene were also usually found. Pentachlorobenzene was also reported in North Sea fish (53) and in fish from Norwegian fjords (7).

Mirex, a perchlorinated cage-structured hydrocarbon, $C_{10}Cl_{12}$, used in southern United States to control the red and black fire ants (Solenopsis invicta and Solenopsis richteri), has been found as a general widespread low-level contaminant in fish from both inland (54, 55, 56, 57, 58) and coastal waters (59). Unexpectedly, in 1974 mirex was also found in Lake Ontario fish from both Canadian (60) and United States (5, 61) waters and in 1978 was measured at levels less than 0.35 ppm wet weight (62, 63). Photomirex (64), $C_{10}HCl_{11}$, a photodegradation product of mirex, was also found in Lake Ontario fish (65, 66). Photomirex in Lake Ontario chinook salmon (Oncorhynchus tshawytscha) averaged 0.13 ppm whole fish and 0.05 ppm red muscle (muscle lateralis superficialis) (67).

Kepone, an oxygenated chlorocarbon of the same skeletal structure as mirex, and a monohydrodechlorination product, $C_{10}HCl_9$, have been found in fish from the James River (68, 69, 70) near Hopewell, Virginia, after the discovery of kepone contamination of the river in 1975. The level of kepone in a 30-mullet-fillet composite was 0.56 ppm, and the level of monohydrokepone was 0.04 ppm (69). Trace levels, less than 1 ppb, of dihydrokepone, $C_{10}H_2Cl_9$, were also reported in James River and Chesapeake Bay fish (71).

Chlordene epoxide (2,3,4,5,7,7-hexachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno[1,2b]oxirene) was identified along with chlordene in catfish obtained from commercial supplies in Louisiana and Texas (72). The levels of chlordene epoxide in three samples were 0.04, 0.30, and 0.27 ppm, whereas the levels of chlordene were 0.00, 0.63, and 0.70 ppm, respectively.

The compound 1-hydroxychlordene has been reported in fish from rivers and lakes in Johnson County, Iowa (73). Johnson County is an agricultural area where tech-chlordane and heptachlor are used extensively on corn crops. 1-Hydroxychlordene ranged from 15 to 75 ppb in 13 species of fish in 1972.

Toxaphene (chlorinated camphene) is used in lakes to control rough fish (74) and has been shown to accumulate in fish where it has been used for this purpose (75). Similarities between components of tech-toxaphene and tech-chlordane often make the identification of components found in environmental samples difficult. Therefore separation of toxaphene from chlordane is often required before analysis (76). Studies of air transport of chlorinated hydrocarbons showed that nearly half of the total high molecular-weight chlorinated organic compounds in the air over the western North Atlantic were toxaphene components (77, 78). The presence of toxaphene therefore, in fish from Lake Vattern, Sweden, where toxaphene has never been used, can possibly be explained by airborne fallout of toxaphene originating in neighboring countries (79).

Polychlorinated terphenyls (PCTs) have been found in oysters and eels from the Rhine river, the Netherlands, at 0.12 ppm and 0.40 ppm, respectively (80). The average level of PCTs in fish collected at 12 sites in the Tama River, Japan, was 0.0025 ppm (81). This value corresponded to only 1/600 the average PCB value. Other samplings of 156 fish (82, 83) and 29 fish (84) from Japanese waters showed no significant level of PCTs. Polychlorinated terphenyls were therefore not considered to be a problem in the aquatic environment (83). In the United States PCTs have been identified in fish from Lake Michigan (85). They have also been identified in both fresh- and saltwater fish from the Slovenia region of Yugolavia (86).

SUMMARY

In preparing this report several hundred papers on polyhalogenated chemical residues in fish have been reviewed. The majority of the papers described either bioassay experiments to determine toxicity or bioaccumulation factors or both, or described chemical-residue monitoring of commonly used herbicides, pesticides, or PCBs. The number of papers reporting unique or unusual chemical residues by chemical-residue characterization procedures was quite small. These reports, however, described a wide variety of polychlorinated chemicals originating from many sources, including direct release of manufactured chemicals from industrial or agricultrual activities, such as kepone in the James River; indirect release of chemicals, such as toxaphene in Lake Vattern, Sweden; release of byproducts of industrial processes, such as polychlorinated styrenes in the Rhine River, and Lake Ontario; and metabolism of environmental contaminants such as DDT to yield dichlorobenzophenone in Lake Michigan.

The importance of these findings however cannot be over emphasized if we are to more fully understand the impact man's use of chemicals has had upon the environment. This review has shown that there exists a large need for continued chemical-residue characterization and the methods developmental work that must accompany it.

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